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(19) (CA) **CANADIAN PATENT** (12)

(54) PROCESS FOR PRODUCING BLEACHED MECHANICAL
PULP HAVING HIGH STRENGTH AND BRIGHTNESS AND
WITH LOW DISCHARGE OF OXYGEN CONSUMING
SUBSTANCES

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The present invention relates to a process for producing mechanical pulp having high strength and brightness.

Mechanical pulp is not an unambiguous concept, but in the present context it is intended to mean refiner mechanical pulp, thermomechanical pulp, chemica-mechanical pulp and semichemical pulp, i.e. pulps produced with a yield higher than 75% based on the wood raw material.

10 Due to the fact that mechanical pulp can be produced with a very high yield based on the wood raw material it is inexpensive and therefore quite attractive and much effort has been invested in improving its quality so as to permit its use in place of the more expensive chemical pulp in many applications. It has become possible to bleach mechanical pulp with, for example, dithionite or peroxides to brightnesses of 82-84% SCAN for hardwood and 74-76% SCAN for softwood.

The greatest drawback for mechanical pulp, however, is that its strength properties are poorer than those of chemical pulp. Its absorbency and softness are also poorer, but this is of less significance in most cases.

20 The reason for the poorer strength of the mechanical pulp is essentially the same as the reason for the higher yield, namely, the higher wood ligning content of the fibres, which means that the flexibility and binding strength are relatively poor. Another factor which contributes to lowering of strength is that the fibres are, to a large extent, shortened by cutting and beating into meal-like fragments in the defibration of the wood. Certain lipophilic substances such as resins and fatty acids and other so-called extractable



substances may, in certain instances, remain in the pulp and influence the strength properties of a finished paper in a negative direction.

In order to come to grips with these problems various methods are employed for softening the wood and thereby the bonds which join the individual fibres, primarily the inter-cellular lignin, to thereby obtain a gentler defibration with accordingly longer and softer fibers.

10 In the thermomechanical process the wood is thus heated with steam and is softened prior to defibration. This may also be combined with various concurrent chemicals such as sulfite solutions having various pH values or peroxides.

Another method for softening the wood is to employ chemicals and a heating restricted to that which is required to obtain a reasonable reaction time. These chemicals include sulfite solutions having various pH values, alkali metal carbonates and/or hydroxides, wherein alkali metal hydroxides, in particular, are very effective in terms of softening. Depending on the reaction time, the amount of
20 chemicals and the temperature, various pulp properties and yields are obtained. Such pulps include chemico-mechanical and semi-chemical pulps, including cold soda pulp.

In practice this chemical treatment can be carried out in a variety of ways, the simplest being to spray the wood, normally in the form of chips, with the chemicals immediately prior to the defibration. Even this simple method produces good results with respect to strength prop-
erties. This is described, for example, in Swedish Patent Application 1850/72 filed by Elektrokemiska Aktiebolager,
30 laid open to public inspection on August 16, 1973.

Another method is to treat the wood in a separate step prior to defibration. The penetration of the softening chemicals into the wood can thereby be improved and the time, temperature and pressure can be varied within wider limits. Examples of such processes would include the cold soda process and the procedures described in Swedish Patent Specifications 303 088 and 226 593 and U.S. Patent Specifications 3 069 309 and 3 023 140.

10 Common to both thermal and chemical softening of the wood prior to defibration is a pronounced darkening of the resulting pulp. If the pulp is to subsequently be bleached by known processes after the softening, the consumption of bleaching agent will be appreciable.

It is possible, and in certain cases even advantageous, to introduce bleaching agent during the thermal and/or chemical treatment, and the above-cited patent specifications describe precisely this procedure. The difficulty with a combined thermal or chemical softening and bleaching is that the optimal conditions for softening rarely or never coincide with the optimal conditions for bleaching. Suitable pH values for the impregnating liquid are 11.0 - 13.5 for softening, while the most suitable pH for peroxide bleaching lies between 8.5 and 11. If the process is directed to maximal softening, there is a pronounced peroxide decomposition because of the high hydroxide ion content, and this must be compensated by increased peroxide if the intended brightness is to be obtained. If, on the other hand, the same softening of the wood is achieved without concurrent introduction of bleaching

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agent and at the same high pH value, the brightness of the resulting pulp will be so low that, as a rule, even larger amounts of peroxide must be used than in the combined instance to produce the same brightness.

The object of the present invention is to achieve an alkali softening of the wood under optimal conditions for softening without a reduction of the pulp brightness. It has been found, quite surprisingly, that even very small charges of peroxide in the form of hydrogen peroxide,
10 organic peroxide or sodium peroxide are sufficient to inhibit, or in any case sharply reduce the darkening of the pulp within the pH interval which is optimal for softening.

In summary it can thus be stated that softening in a first step with strong alkali produces a strong pulp, but without softening the fibres are broken and the pulp becomes weaker. If a small amount of hydrogen peroxide is added to the alkali the darkening is prevented and the subsequent bleaching at a lower pH is facilitated.

Thus, according to the invention, there is provided a
20 process for continuously producing bleached mechanical pulp from lignocellulosic material which comprises: (a) softening lignocellulosic material in a separate impregnation step with a peroxide-containing solution of alkaline hydroxides in an amount such that the pH is above 11 but not more than about 13.5; (b) passing the thus-softened material into a bleaching stage where a peroxide-containing solution is added and the pH is maintained below 11 but not less than about 8.5; (c) adjusting the amount of peroxides added to the system so that from 10 to 30 per cent of that totally
30 required is added in said softening stage and the balance in said bleaching stage; and (d) performing mechanical

disintegration of the material to pulp in at least one defibrating apparatus after the softening treatment.

It has, of course, been previously established that a high pH results in peroxide decomposition and a logical measure has therefore been to divide up the peroxide charge between the softening pretreatment step and defibration.

Such attempts have been made and are described in the above-cited patent specifications and in Pulp and Paper Magazine of Canada, Vol. 73, 1972, p. 80, but therein at
10 least 75% of the total peroxide was added in the pre-treatment step and the remainder to a separate bleaching step or to the refiner after the softening step. In all instances the wholly differing pH

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optima of the partial processes have been ignored.

What is thus surprising in our present invention is not that the charged peroxide is better utilized if it is divided up into several steps, but rather that the peroxide charge in the pretreatment step can be held so low. The best result is namely achieved at a charge as low as even 103-0% of the total required peroxide to the softening step, and in no case has it been found necessary to go as high as 75%.

10 Pretreatment is carried out to the point where the falling pH value permits a true bleaching to take place, and it is therefore advantageous to place a bleaching tower directly after the refiner for final bleaching of the pulp.

The required pH reduction from the softening step to the bleaching step can only be achieved, in most cases, by controlling the residence time and the temperature during the pretreatment so that the correct pH for the bleaching is obtained. It is, of course, possible to lower the pH when required by adding an acid such as sulfate solution, sulfuric acid or acidic white water from another fabrication step. In
20 order to achieve an effective mixture of the bleaching agent, the agent can be introduced before the refiner since the refiner acts as a very effective mixer.

Because the peroxide charge to the pretreatment step is so low, the residual peroxides from the subsequent bleaching step are often sufficient for charging to the pretreatment step. The reason why such a small amount of hydrogen peroxide is required in the pretreatment is not fully understood, but it may depend on the fact that released carbohydrate acids in

the pretreatment step, and if recycling is used, also from the bleaching step act as complexing or chelating agents for heavy metals in the wood and thereby stabilize the peroxide. A recycling of waste liquor from the bleaching step to the pretreatment step also sharply reduces the amount of released oxygen consuming substance.

10 With this point of departure attempts have also been made to additionally introduce chelating agents to the hydrogen peroxide in the pretreatment step. Chelating agents from the detergent field, NTA, EDTA, DTPA, i.e. nitrilotriacetic acid, ethylene diaminetetraacetic acid and diethylenetriaminopentaacetic acid, and tripolyphosphates, i.a. have been investigated.

20 According to the invention optimal strength is thus obtained for the pulp with a pretreatment step which is carried out without loss of brightness and with a minimal amount of peroxide. The subsequent bleaching is performed by known means in a refiner and/or in a bleaching tower, and since the pulp prior to the actual bleaching step already has a high brightness and since the bleaching step can, in addition, be carried out under optimal conditions, a high brightness is obtained at maximal strength for the pulp with a minimal consumption of peroxide.

The possibility of controlling the charges of alkali and hydrogen peroxide independently allows all reaction conditions to be held at optimal levels. Prior processes have utilized alkali and hydrogen peroxide in a constant ratio and a charge, for example, of sodium peroxide alone produces a constant ratio of 1/2 mol hydrogen peroxide per mol sodium peroxide.

The invention is illustrated by the following examples wherein the same test procedure is used in all tests. The different variables are presented in the table below in which tests 1-10 represent spruce and 11-14 hardwood. Tests 1, 2, 5, 7, 13 and 14 are comparative examples according to the prior art while the remaining tests are performed according to the invention.

10 In all tests match chips having a dimension of 25 x 3 x 3 mm are placed in a steel vessel which is then evacuated. The chemicals together with water are drawn into the wood and a hydraulic overpressure of 6 bar is thereafter applied. Unless otherwise indicated the impregnation period is 1 hour and the impregnation temperature is 45°C. 41° Bé water glass in an amount corresponding to 4.5% based on the wood is introduced in all cases in connection with the alkali charging.

After the pretreatment the chips are defibrated to 100 ml freeness Canadian Standard in a laboratory defibrator.

20 The bleaching step is made so that additional chemicals are added, in part, to the defibrator during defibration, and , in part, separately after defibration. The pulp concentration during bleaching is 15%, both in the defibrator bleaching and the separate bleaching. In the separate bleaching after defibration the residence time is 2 hours and the temperature 70°C. When the bleaching is done as defibrator or refiner bleaching the pulp is stored at 70°C after defibration so that the total residence time is 2 hours.

Table I

Exp. No.	Pretreatment		Defibration		Bleaching			Paper Qualities		
	NaOH %	H ₂ O ₂ %	NaOH %	H ₂ O ₂ %	NaOH %	H ₂ O ₂ %	R-H ₂ O ₂ %	Bright-ness, % SCAN	Tear Index	Breaking Length, km
5	1	1.0	4.3				20	75.1	34	1.57
	2	1.0			0.1 ⁺⁾	4.3	18	74.3	35	1.56
	3	1.0	1.0		0.2 ⁺⁾	3.3	34	76.2	35	1.61
	4	4.5	4.5				10	72.9	38	3.2
10	5	4.5				4.5	17	69.8	40	3.1
	6	4.5	1.0			3.5	35	74.2	41	3.1
	7	4.5	3.5			1.0	12	72.3	40	3.1
	8	4.5	0.8 ⁺⁺⁾			3.7	38	74.1	41	3.0
15	9	4.5	0.8 ⁺⁺⁾	3.7			34	74.0	40	3.2
	10		4.5	1.0		3.5	40	73.5	35	2.9
	11	+++)	+++)	1.0	1.1		2.5	35	81.5	-
	12	2.0	1.0			2.5	32	83.1	-	-
	13	2.0				4.5	19	78.1	-	-
	14	2.0	4.5				20	78.0	-	-

20 ⁺⁾ To obtain the correct initial pH in the bleaching step.

⁺⁺⁾ Recycled residual peroxides from Example 6.

⁺⁺⁺⁾ Pretreatment at 110°C and 0.5% SO₃²⁻ charge. Time about 5 min.

25 Depending on the wood, the type of wood and the desired type of pulp the chemical charges can vary within wide limits and the examples show brightness variations for comparable bleaching agent charges. The strength values obtained apply to samples prepared in a laboratory refiner and must thus be seen

as illustrations of the impressive improvement in strength when the alkalinity in the softening step increases.

5 The test series clearly shows the appreciable increase in brightness obtained according to the invention in spite of the high alkali charges. Tests 8 and 9 deserve special mention. The peroxide demand to the softening step is completely covered by the residual peroxides in the waste spent liquor from the final bleaching step.

10 Test 11 shows that the invention can also be applied to thermomechanical pulp.

The present invention is not limited to embodiments with a special pretreatment apparatus. Pretreatment apparatus is herein intended to mean any wood impregnation equipment with or without heating, such as cellulose digesters, pressure vessels with or without screw feed, chip washing with a closed washing fluid system, vibrating chip processers such as "live bottom bins", etc. The application can as well take place with direct softening in the first defibration step and further bleaching in a second refiner step or a separate bleaching step on a combination of other refiner and bleaching steps. This is illustrated by tests 9, 10 and 11. What is essential is that the softening takes place at a pH higher than 11 in the presence of relatively small amounts of peroxide and that the actual bleaching thereafter occurs at pH values less than 11 with charging of additional peroxide.

25 The invention also has a beneficial effect on the release of oxygen consuming substance, BS_7 , from the process. In bleaching two samples of refiner pulp, half of the white

water from the first sample was used as dilution water in the second sample. 4% hydrogen peroxide, 4% water glass and 1.4% caustic soda were used in the test. The bleaching temperature was 60°C, the bleaching time 2 hours and the concentration 10%.

5 The values obtained for oxygen consumption are seen in Table 2 below.

Table 2

Ex. No.	BS ₇ in waste liquor kg/t	Recycled BS ₇ kg/t	New BS ₇ kg/t
10 1	15.6	0	15.6
2	16.5	7.6	8.9

From the values it may be seen that the application of the invention reduces the new formation of oxygen consuming substances to about half.

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Even lignocellulose material other than softwood and hardwood such as grass, bamboo, bagasse, etc. can be used for pulp production according to the invention.

SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for continuously producing bleached
mechanical pulp from lignocellulosic material which comprises:

(a) softening lignocellulosic material in a separate
impregnation step with a peroxide-containing solution of
alkaline hydroxides in an amount such that the pH is above
11 but not more than about 13.5;

(b) passing the thus-softened material into a bleaching
stage where a peroxide-containing solution is added and the pH
is maintained below 11 but not less than about 8.5;

(c) adjusting the amount of peroxides added to the system
so that from 10 to 30 per cent of that totally required is
added in said softening stage and the balance in said bleaching
stage; and

(d) performing mechanical disintegration of the material
to pulp in at least one defibrating apparatus after the
softening treatment.

2. A process according to claim 1 wherein the adjustment
of peroxide supply between the two stages is accomplished by
withdrawing spent peroxide-containing liquor from the bleaching
stage and adding it to the softening stage.

3. A process according to claim 1 wherein the bleaching
stage is performed in the defibrating apparatus.

4. A process according to claim 1 wherein the bleaching
stage is performed in a separate tower immediately after the
defibrating apparatus.

5. A process according to claim 1 in which said ligno-
cellulosic material is chopped prior to said softening step.



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ABSTRACT OF THE DISCLOSURE

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The invention relates to a process for producing bleached mechanical pulp having improved strength and brightness by mechanical decomposition of material softened by thermal and/or chemical processing and bleaching with a small amount of peroxide containing bleaching agent with the formation of small amounts of oxygen consuming substances in the waste liquors. According to the invention the wood is softened in a first step at high pH with introduction of 10 - 30% of the peroxide required for the bleaching, i.e. only sufficient peroxide to prevent the pulp from darkening during the softening step. The subsequent bleaching takes place at low pH with the addition of the remainder of the peroxide, optionally with the introduction of agents which amplify the action of the peroxide on the wood, such as complexing or chelating agents and/or surfactants.

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